Studies on natural rubber-bound diphenylamine antioxidants

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Diphenylamine was chemically attached to depolymerised natural rubber by photochemical reaction. The rubber-bound diphenylamine was characterised by TLC, HNMR, IR and TGA. The efficiency and permanence of the bound diphenylamine was compared with conventional amine type antioxidant in natural rubber vulcanizates. The rubber-bound diphenylamine was found to be less volatile and less extractable compared to the conventional antioxidant. The vulcanizates showed improved ageing resistance in comparison to vulcanizates containing conventional antioxidant. Also, the presence of liquid rubber-bound diphenylamine reduces the amount of plasticiser required for compounding.

INTRODUCTION

Service requirements placed on finished rubber products demand improved polymer stabilisation. Many amine and phenolic antioxidants are commercially available. Serious drawbacks of all antioxidants existing today are volatility and extractability. The decrease in concentration of the antioxidants impairs the resistance to degradation. One method to increase the persistance of the antioxidant in polymers is to chemically attach the antioxidant to the rubber. The potential advantages of these polymer-bound antioxidants are that they cannot migrate to the rubber surface and hence cannot be lost by volatilisation or solvent leaching.[1,2] Cane et al.[3] have shown that mobility of the antioxidant is not essential for heat ageing or oxidative ageing, but will become essential for protection against ozone attack or dynamic fatigue.

Polymerisable monomeric antioxidants were described by Tamura and coworkers.[4,5] Preparation of bound phenyl-β-naphthylamine by the reaction of naphthylamine with rubber modified with dichlorocarbene was described by Kirpichev & Yakubchik.[6] The most versatile method of preparation of bound antioxidant is by the direct reaction of conventional antioxidants with rubber. Scott et al. have demonstrated that simple hindered phenols which contain a methyl group in the *ortho* or *para* position, can react with natural rubber in the presence of oxidising free radicals to yield polymer-bound antioxidants.[7-9] Antioxidants like styrenated phenol, diphenylamine, etc., bound to hydroxy-terminated liquid natural rubber by a modified Friedel–Craft's reaction, were also found to be effective in improving ageing resistance.[10] This paper describes chemical binding of diphenylamine to natural rubber by a photochemical reaction. This rubber-bound antioxidant was compared with conventional antioxidants in filled natural rubber compounds.

EXPERIMENTAL

Materials

Natural rubber (NR) (ISNR-5, Mooney viscosity ML(1 + 4) 100°C-82) was supplied by the Rubber

Rubber Research Institute of India, Kottayam. Compounding ingredients, zinc oxide, stearic acid, aromatic oil and carbon black (HAF N 330), were commercial grade. Mercaptobenzothiazole (MBT) and Tetramethylthiuramdisulphide (TMTD) were rubber grade—supplied by Bayer India, Ltd. Methanol, acetone and toluene were of reagent grade and used as such. Diphenylamine (DA) (Analar grade) from E. Merck, India, was used. Commercial antioxidant, Pilflex-13 (substituted paraphenylenediamine) was supplied by Poly Olefins Ltd, India.

Preparation of NR-bound DA

NR was masticated for 30 min at 50°C. A 100 g sample of this was dissolved in 1 litre of toluene and the solution was charged into a flat-bottomed glass flask (wide neck, 16 cm in diameter) of 2 litre capacity with quartz windows. It was fitted with a mechanical stirrer and covered with a quartz lid. The whole assembly was placed in sunlight (for UV-radiation). After 60 h exposure, 25 g DA dissolved in toluene was added. The sample was divided into 10 equal portions and was again placed in sunlight. Samples were taken after 1, 2, 3, 4, 5, 6, 7, 10, 12 and 15 h of exposure and poured into excess methanol; with stirring, liquid rubber was precipitated. The unreacted DA was removed by repeated re-precipitation, and the product was dried in vacuum. The rubber-bound antioxidant was obtained as a viscous liquid. Samples taken after different times of exposure were added to NR compounds according to the formulation given in Table 1. The optimum exposure time for preparing

Table 1. Composition of test samples

Sample	X	A	B
Natural rubber (phr)	100	100	100
Zinc oxide	5·0	5·0	5·0
Stearic acid	2·0	2·0	2·0
Mercaptobenzothiazole	0·6	0·6	0·6
Tetramethylthiuramdisulphide	0·2	0·2	0·2
Sulphur	2·5	2·5	2·5
Carbon black HAF (N 330)	40·0	40·0	40·0
Aromatic oil	5·0	3·0	5·0
Pilflex-13	—	—	1·0
NR–DA	—	5·0	—
Cure characteristics			
Cure time (min)	2·6	3·1	2·9
Scorch time (min)	2·1	2·6	2·3

phr: parts per hundred rubber.
NR–DA: DA bound to depolymerised NR.

rubber-bound antioxidant was determined by studying the retention in tensile strength after ageing the vulcanizates at 100°C for 48 h. Maximum retention in tensile strength was obtained for vulcanizates containing the rubber-bound samples produced by exposure for 6 h and above. The time of exposure to sunlight was thus fixed as 6 h.

Analysis of the rubber-bound antioxidant

Analysis of the bound antioxidant was carried out by using thin layer chromatography (TLC), gel permeation chromatography (GPC), infra-red spectroscopy (IR), proton magnetic resonance spectroscopy (^{1}H NMR), and thermogravimetric analysis (TGA). TLC was carried out using silica gel as the absorbent. A mixed (benzene and ethyl acetate; 4: v/v) was used as the developing solvent for all samples while ninydrin was used as the colour developing agent for the antioxidants and iodine for NR.[11]

The molecular weight of the NR–DA was estimated by gel permeation chromatography (Water Associates, Model 6000) employing a differential refractometer R-401, and polystyrene standards.

IR spectra were taken on a Beckman spectrometer.

The ^{1}H NMR measurements were carried out using a Hitachi Perkin-Elmer R-243 (60 MHz) Model. Spectra were measured at 20°C with 10 wt% solutions of the samples in CCl$_4$, with tetramethylsilane as the internal standard.

Thermogravimetric analysis (TGA) was carried out using a Dupont TG-DSC standard model in nitrogen atmosphere at a heating rate of 10°C min^{-1}.

The optimum concentration of the rubber-bound antioxidant for maximum retention in properties was determined by varying the amount of antioxidant in the mix from 1 to 8 phr.

This chemically bound DA was added to NR according to the formulation given in Table 1. The amount of plasticiser can be reduced by the use of liquid rubber-bound antioxidant as shown in Table 1. The optimum cure times (time to reach 90% of the maximum torque) and scorch times (time to reach 10% of the maximum torque) of the compounds were determined in a Göttfert Elastograph, model 67.85, as per ASTM D-1646 (1981).

Rubber compounds were moulded in an

electrically heated laboratory hydraulic press, at 150°C, up to their optimum cure time. Dumb-bell shaped tensile test pieces were punched out of these compression moulded sheets along the mill grain direction. The tensile properties of the vulcanizates were evaluated on a Zwick Universal Testing Machine, model 1445, using a crosshead speed of 500 mm min^{-1} as per ASTM D-412-80. Tear resistance of the vulcanizates was evaluated as per ASTM D 624-81 using un-nicked 90° angled test specimens. The ageing resistance of the vulcanizates was studied by ageing for 12, 24, 36 and 48 h at 100°C, then measuring the retention in tensile properties. The extractability of the bound antioxidant was studied by keeping the samples in methanol and acetone for 48 h at room temperature. The retention in tensile properties was again evaluated after ageing the samples at 100°C for 12, 24, 36 and 48 h.

RESULTS AND DISCUSSION

Figure 1 shows the variation in tensile strength after ageing at 100°C for 48 h with exposure time after addition of DA into the partially depolymerised NR solution. The retention in properties increases first, reaches a maximum, and then levels off at an exposure time of 6 h. This shows that after an optimum time of exposure, all the DA molecules get attached to the depolymerised NR.

Figure 2 shows the TLC of DA-depolymerised NR (sunlight-irradiated for an equivalent time) and DA bound to NR. NR was not coloured by ninhydrin while NR–DA and DA were coloured. the Rf value of NR–DA was found to be almost equal to that of depolymerised NR. This shows
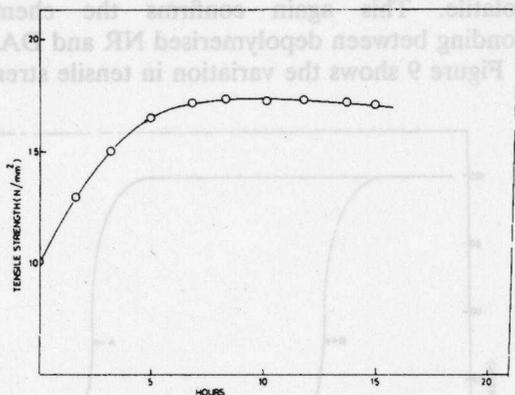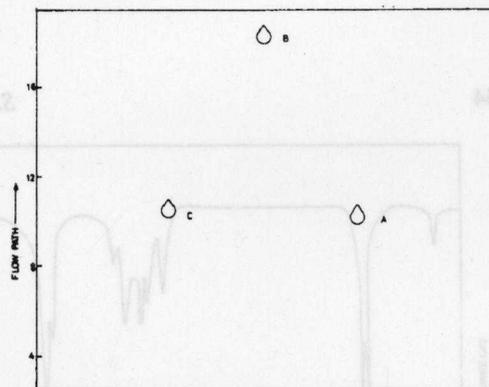
Fig. 2. TLC of compounds: A—NR–DA, B—B–DA C—depolymerised NR.

that DA gets chemically bound to depolymerised NR during sunlight irradiation.

Figure 3 shows the GPC traces of depolymerised NR and DA attached to depolymerised NR—referred to as NR–DA. The molecular weight of NR–DA (mol. wt—2300) is found to be very close to that of depolymerised NR (mol. wt—2245).

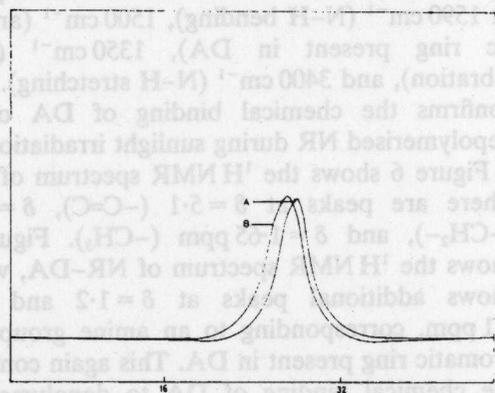Figures 4 and 5 show the IR spectra of NR and

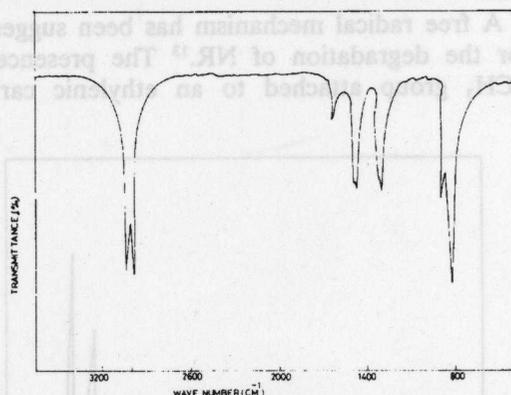**Fig. 3.** GPC traces: A—depolymerised NR, B—NR–DA.

Fig. 1. Variation of tensile strength with exposure time.

Fig. 4. IR spectrum of depolymerised NR.

Fig. 5. IR spectrum of NR–DA.

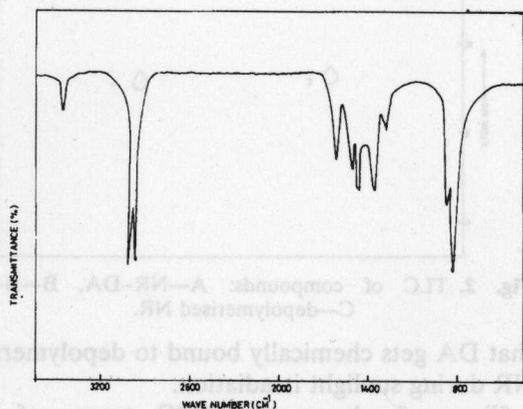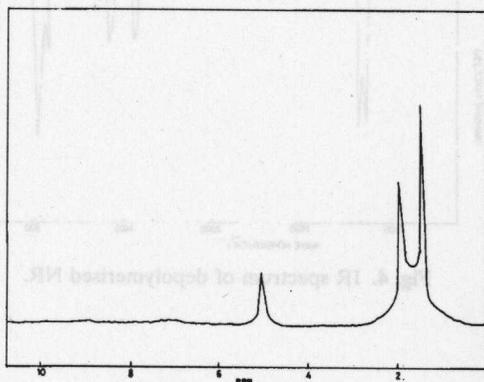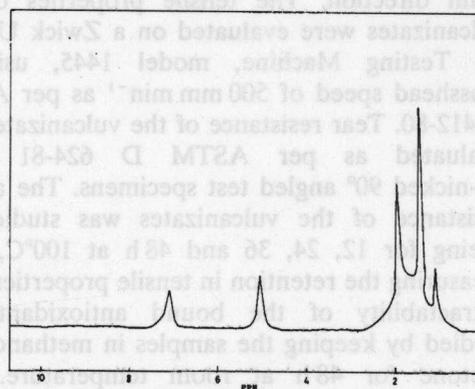**Fig. 7.** ¹H NMR spectrum of NR–DA.

NR–DA. The IR spectrum of NR shows the peaks at 3000 cm⁻¹, corresponding to aliphatic C–H; 1665 cm⁻¹ due to =C=C=; 1400 cm⁻¹ due to –CH₃; and 835 cm⁻¹ due to –C(CH₃)=CH–. The IR spectrum of NR–DA shows additional peaks at 1590 cm⁻¹ (N–H bending), 1500 cm⁻¹ (aromatic ring present in DA), 1350 cm⁻¹ (C–N vibration), and 3400 cm⁻¹ (N–H stretching). This confirms the chemical binding of DA on to depolymerised NR during sunlight irradiation.[12]

Figure 6 shows the ¹H NMR spectrum of NR. There are peaks at δ = 5·1 (–C=C), δ = 1·22 (–CH₂–), and δ = 1·65 ppm (–CH₃). Figure 7 shows the ¹H NMR spectrum of NR–DA, which shows additional peaks at δ = 1·2 and δ = 7·1 ppm, corresponding to an amine group and aromatic ring present in DA. This again confirms the chemical binding of DA to depolymerised NR.

A free radical mechanism has been suggested for the degradation of NR.[13] The presence of –CH₃ group attached to an ethylenic carbon

atom in isoprene tends to reduce the –C–H dissociation energy by hyperconjugation.[14] During sunlight irradiation the impurities present in NR solution undergo photolysis and the resulting radicals will abstract the –C–H proton, giving rise to macro alkyl radicals (No. I). These radicals will react with oxygen, leading to the formation of hydroperoxide.[15–17] The decomposition of these hydroperoxides results in the formation of alkyl radicals (No. II). Based on the complex transformations of aromatic secondary amines during ageing in the presence of a substituted hydrocarbon, and from the mechanism of degradation of NR, the following mechanism can be suggested for the attachment of DA on to depolymerised NR.[13,14,16–18]

Figure 8 shows the thermograms of DA and NR–DA. The low molecular weight DA volatilises easily while rubber-bound DA is less volatile. This again confirms the chemical bonding between depolymerised NR and DA.

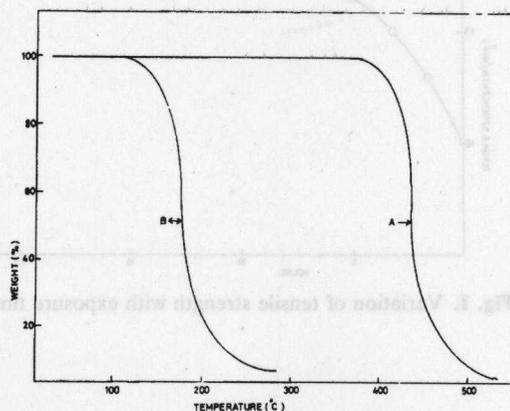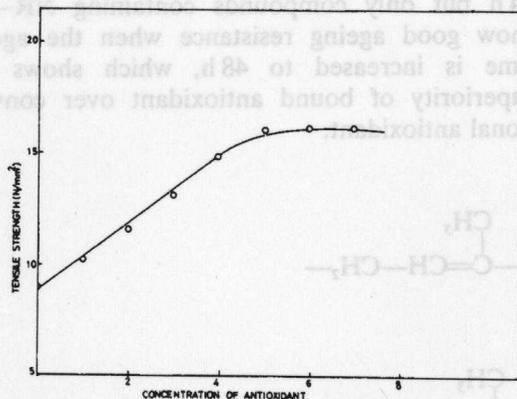Figure 9 shows the variation in tensile strength

Fig. 6. ¹H NMR spectrum of NR.

Fig. 8. TGA of compounds: A—NR–DA, B—DA.

after ageing with a concentration of antioxidant. The tensile strength retention is found to increase with the amount of chemically bound antioxidant, reaches a maximum, and then levels off. The higher amount required of bound antioxidant, in comparison to conventional antioxidant, may be due to a lower amount of effective antioxidant in the rubber-bound product.

Figure 10 shows the tensile strength of the vulcanizates of the compounds shown in Table 1 before and after ageing. All the vulcanizates show fairly good resistance to ageing at 100°C for 24 h but only compounds containing NR–DA show good ageing resistance when the ageing time is increased to 48 h, which shows the superiority of bound antioxidant over conventional antioxidant.

Scheme 1

Figure 11 shows the change in elongation-at-break of the vulcanizates before and after ageing. The compound containing NR–DA shows better retention in elongation-at-break after ageing. This again shows that the bound antioxidant can improve the ageing resistance of NR compounds.

Figure 12 shows the variation in tear strength of the vulcanizates before and after ageing. It further confirms the superiority of the bound antioxidant.

Figure 13 shows the variation in modulus of the vulcanizates before and after ageing. The increase in modulus after 24 h ageing may be due to co-crosslinking of the chemically-bound antioxidant with NR.

Figures 14 and 15 show the variation in tensile strength and elongation-at-break of the vulcanizates (of the compound shown in Table 1) before and after ageing, after extracting the samples in acetone and methanol. The retention in prop-

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Fig. 9. Variation of tensile strength with concentration of the antioxidants.

Fig. 11. Variation of elongation-at-break of the vulcanizates before and after ageing: A—NR–DA, B—Pilflex-13, X—without antioxidant.

Fig. 10. Variation of tensile strength of the vulcanizates before and after ageing: A—NR–DA, B—Pilflex-13, X—without antioxidant.

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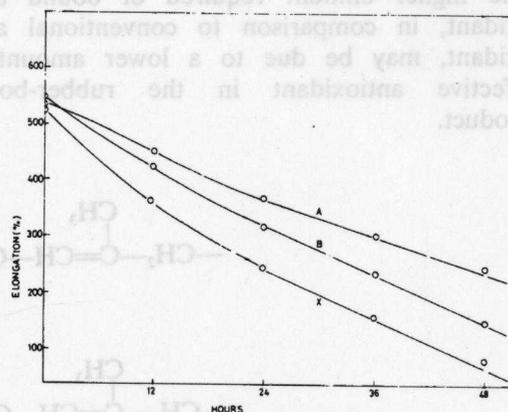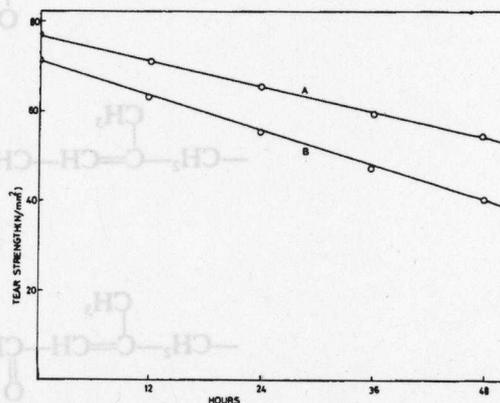

Fig. 12. Variation of tear strength of the vulcanizates before and after ageing. A—NR–DA, B—Pilflex-13.
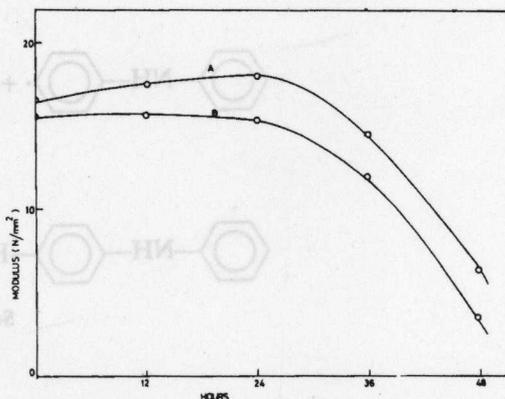

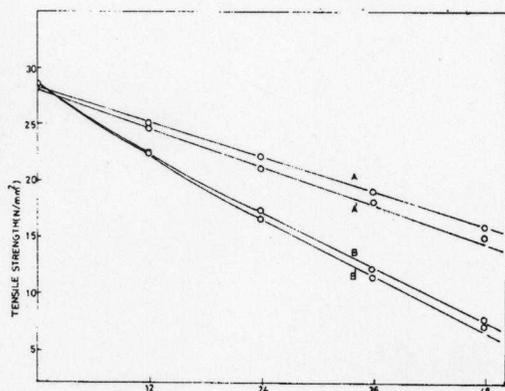**Fig. 13.** Variation in modulus of the vulcanizates before and after ageing: A—NR–DA, B—Pilflex-13.

Fig. 14. Variation of tensile strength of the vulcanizates before and after ageing, after extracting the samples: (a) in methanol (A—NR–DA, B—Pilflex-13) (b) in acetone (A′—NR–DA, B′—Pilflex-13).
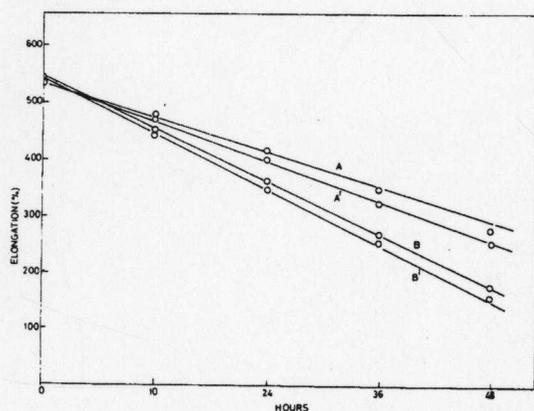

Fig. 15. Variation of elongation-at-break of the vulcanizates before and after ageing, after extracting the samples: (a) in methanol (A—NR–DA, B—Pilflex-13); (b) in acetone (A′—NR–DA, B′—Pilflex-13).

erties by the vulcanizates containing NR–DA is probably due to the lower extractability of the bound antioxidant by the solvents.

CONCLUSIONS

DA can be chemically attached to depolymerised NR by photochemical reaction.

The rubber-bound antioxidant has superior resistance to evaporation and extraction compared to conventional antioxidants. Also, it can improve the ageing and can reduce the amount of plasticiser required for compounding.

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